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Perspectives of carbon nanotubes/polymer nanocomposites for wind blade materials



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ABSTRACT

The global market for wind energy has increased exponentially in the past few decades, and there is a continuous effort to develop cost-effective materials with higher strength to mass ratio for wind blades. With unique structural and transport properties, carbon nanotubes (CNTs) have attracted much interest as the reinforcement to develop polymer-based nanocomposites delivering exceptional mechanical properties and multi-functional characteristics. In light of previous and current status in carbon-based materials, herein the suitabilities of CNT/polymer nanocomposites for wind blade materials are analyzed. Special emphasis is placed on the mechanical, fatigue, electrical, thermal and barrier properties of CNT/polymer nanocomposites, which are important considerations when selecting suitable materials for wind blades with larger rotary radius. The application of CNT/polymer nanocomposites as sensory materials for the monitoring of defects in composite structures is also discussed. Finally, based on the progress made so far, some suggestions paving the way for the large commercialization of these nanocomposites for wind blades are presented.

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Contents

| | | uction | | | | |
|-----|---|--|-----|--|--|--|
| 2. | Suitabilities and advantages of CNT/polymer nanocomposites for wind blade materials | | | | | |
| | 2.1. | Material requirements to wind blades | 653 | | | |
| | 2.2. | Strategies to improve the performance of wind blade materials using CNTs | 654 | | | |
| | 2.3. | Mechanical reinforcement | 654 | | | |
| | | Environmental issues. | | | | |
| | 2.5. | Barrier performance | 656 | | | |
| | | Defect monitoring in FRP structures. | | | | |
| | | usions and perspectives | | | | |
| Ack | Acknowledgments | | | | | |
| Ref | erences | | 660 | | | |

1. Introduction

Wind power, the conversion of wind energy into a useful form of energy, has become an increasingly attractive source of energy generation in past three decades. As an alternative to fossil fuel,

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wind power is in characteristic of plentiful, renewable, widely distributed, clean, and producing no greenhouse gas emissions during the generation and operation. In 2012 the world wind capacity reached 282 GW, growing by 44 GW over the preceding year, and the distribution by top 10 countries is shown in Fig. 1A [1]. All wind turbines installed by the end of 2012 worldwide can provide 580 TW per annum, which is more than 3% of the global electricity demand [2]. It is predicted that the total wind electricity will increase rapidly in next 15 years, with the fastest development of new capacity taking place in China and India [1,2].

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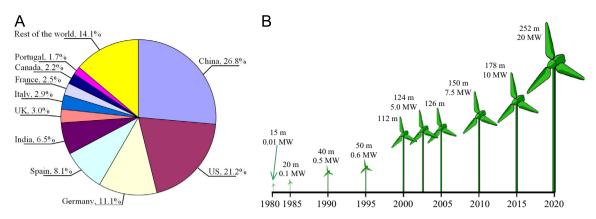


Fig. 1. (A) Distribution of wind power capacity produced by top 10 countries in 2012; and (B) development of wind turbine with larger rotor diameter and higher power capacity since 1980 [1–4].

Table 1Physical and applicable properties of different carbon-based materials [5].

| Properties | Carbon materials | | | | | |
|---|---|------------------------|--------------------|------------------------|---------------|--|
| | Graphite | Diamond | Fullerene | Carbon fiber | CNT | |
| Specific gravity (g/cm³) | 1.9-2.3 | 3.5 | 1.7 | 1.8-2.1 | 0.8-1.8 | |
| Tensile modulus (GPa) | 1000 ^a 36.5 ^b | 500-1000 | 14 | 100-500 | 1000 | |
| Tensile strength (GPa) | $\sim 10^{a} < 0.01^{b}$ | 1.2 | N/A | 1.0-5.6 | > 10 | |
| Electrical conductivity (S/cm) | 4000 ^a 3.3 ^b | $10^{-2} - 10^{-15}$ | 10-5 | $10^2 - 10^4$ | $10^2 - 10^6$ | |
| Electron mobility (cm ² /(V s)) | $\sim 10^4$ | 1800 | 0.5-6 | $10^2 - 10^4$ | $10^4 - 10^6$ | |
| Thermal conductivity (W/(m K)) | 298 ^a 2.2 ^b | 900-2320 | 0.4 | 21-180 | 2000-6000 | |
| Coefficient of thermal expansion (K^{-1}) | -1×10^{-6a} 2.9×10^{-5b} | $(1-3) \times 10^{-6}$ | 6.2×10^{-5} | $\sim\!1\times10^{-6}$ | Negligible | |
| Thermal stability in air (°C) | 450-600 | < 600 | < 600 | 500-600 | > 650 | |
| Cost/Price (US\$/g) | 0.01-0.002 | > 100 | 40-70 | 0.02-0.1 | 0.3-10 | |
| General content in polymer matrix (wt%) | > 10 | > 5 | > 1 | > 10 | < 0.5 | |

^a In-plane.

In order to achieve the expansion expected in this area, there is a strong need for the development of stronger and lighter materials which enable the manufacturing of wind blades with larger rotors. Theoretical and engineering practices have proven that the larger the area through which the wind turbine can rotate, the more wind energy that can be captured, as schematically shown in Fig. 1B [3]. In addition, leading manufacturers of wind blades generally guarantee that the lifetime of products is approximately 20 years [4]. To extend the working lifetime of blades and enable larger area rotors to be cost-effective, it is necessary to design and optimize blade materials to be much stiffer, stronger, and exhibit better fatigue resistance than currently used ones.

The emergence of nanotechnology as a major field of research, especially based on carbon nanotubes (CNTs), has impacted almost every scientific discipline. Different from other carbon materials, such as graphite, diamond and fullerene (C_{60} , C_{70} , etc.), CNTs are one dimensional carbon materials with a tube-like structure which can have a length-to-diameter ratio greater than 1000. Theoretically, this material can be envisioned as cylinders composed of rolled-up graphite planes with diameters in nanometer scale. The cylindrical nanotube usually has at least one end capped with a hemisphere of fullerene structure [5].

With this unique structure and inherent nature of carbon material, CNTs exhibits some properties which are distinctive from other carbon allotropies. Table 1 summarizes the physical and applicable properties of different carbon-based materials [5]. It is clear that CNTs have many advantages over other carbon materials,

offering CNTs great potential to develop high performance material for various applications.

Wood and canvas were used at the early stage of windmills due to their low price, availability, and ease of manufacture. Small blades can also be made from light-weight metals like aluminum and its alloys. These materials, however, require frequent maintenance and limit the blade shape to be a flat plate, which has a relatively low aerodynamic efficiency to capture wind energy [6]. Polymer composites, consisting of additives and polymer matrices including thermoplastics, thermosets and elastomers, are considered to be an important group of relatively inexpensive materials for many engineering applications. These materials are also the fundamental for the structure of modern wind blades. Constituent materials with different properties are selected to fabricate polymer-based composites to improve one or more properties: for example, nature or man-made fibers are introduced into polymer matrices to fabricate composites that have enhanced mechanical and fracture properties. However, there are bottlenecks in optimizing the properties of polymer composites by employing traditional microscale fillers, the reasons are two-folds: (i) The content of conventional filler in polymer composites is generally in the range of 10-70 wt%, giving rise to a higher density than that of the neat polymer matrix; and (ii) stiffness of polymer composites is often traded for toughness, and microscopic defects and voids arising from the high volume fraction of filler often lead to premature failure of the composites [7].

The introduction of nanoscale CNTs as an additive into a polymer resin results in CNT/polymer nanocomposites. Different

^b c-Axis.

from the traditional polymer composites containing microscale fillers, the properties of nanocomposites can be changed significantly even at an extremely low filler content. For example, the electrical conductivity of CNT/epoxy nanocomposites can be enhanced by more than 10 orders of magnitude with less than 0.5 wt% of CNTs [8]. The excellent electrical, thermal and mechanical properties combined with many desirable functional properties of CNTs (see Table 1) provide huge potential applications of CNT/polymer nanocomposites. In addition, CNT/polymer nanocomposites are one of the most extensively studied composite systems partly because low-cost processes are widely available for the manufacturing of composites [5].

This paper is a part of a large project on the development of multi-functional polymer nanocomposites for engineering and environmental applications. In this paper, the perspectives of CNT/polymer nanocomposites for wind blade are analyzed with considerations on the structural and functional requirements for blade materials. Suggestions and challenges for the application of these nanocomposites in wind blades are presented.

2. Suitabilities and advantages of CNT/polymer nanocomposites for wind blade materials

2.1. Material requirements to wind blades

Wind blade represents the most important part in a wind turbine, and its properties play a dominant role in determining the overall performance and lifetime of the turbine. Indeed, the rotor component covers approximately 20% of a wind turbine cost. In service life, wind

blades are subject to various external loading conditions [9,10], including the flapwise and edgewise bending loads, gravitational loads, inertia forces, loads due to pitch acceleration and torsion. The flapwise and edgewise bending loads cause tensile and compressive stresses for the materials, respectively. In addition, the flapwise and edgewise bending moments also lead to the growth of fatigue damages in materials, and these two moments are responsible for more than 90% of the damage in blades. Besides the aforementioned loading conditions, the wind blades are also subject to the cyclic loadings caused by wind variations, turbulences, wind shear, and pressure variations of air around the wind tower, and so forth.

The combined loading conditions for wind turbines make the selection of constitute materials for blades a challenge task. Significant progress has been made to evaluate and optimize the properties of blades made from a variety of materials, ranging from synthetic polymers (thermoplastics and thermosets) to nature polymers (wood). Ideal materials for high performance blades should satisfy some requirements, as shown in Fig. 2. They include the followings [9–11]: (i) low weight (or density) to reduce the load on the tower, and the effect of gravitational forces generated due to the weight of materials; wide availability and easy processing of materials to reduce the cost and maintenance; (ii) high strength of materials to withstand strong wind under the harsh conditions, as well as the gravity load arising from the blade material itself; (iii) high fatigue resistance and reliability of materials to ensure the stable functioning during the service life; (iv) high stiffness to ensure the stability of the aerodynamically optimal shape and orientation of the blade during the work time, as well as clearance between blade and the tower; and (v) excellent stability to address the issues arising from environmental impacts, like lighting strikes, humidity, temperature, etc.

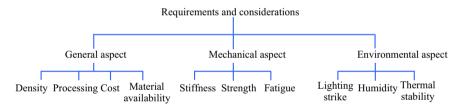
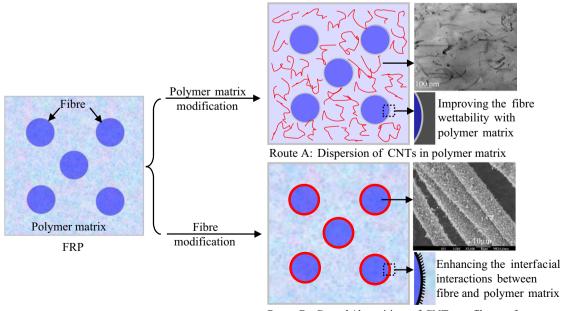


Fig. 2. Material requirements and considerations for high performance wind blades.



Route B: Growth/depositi on of CNTs on fibre surface

Fig. 3. Strategies to improve the performance of FRPs using CNTs.

2.2. Strategies to improve the performance of wind blade materials using CNTs

Nearly all commercialized wind blades are made from fiber reinforced polymers (FRPs), a composite material consisting of a polymer matrix and continuous fibers (Fig. 3). In FRP structure, long fibers ensure longitudinal stiffness and strength, while the polymer matrix is responsible for the fracture toughness, delamination strength, out-of-plane strength and stiffness of the materials.

Based on the components of FRPs, efforts aiming at enhancing the performance of wind blades can be put on modifying the properties of either polymer matrix or fiber. Specifically, CNTs can be incorporated into the materials for wind blades via the following two ways: (i) adding CNTs into polymer resins through proper dispersion and processing [12], and the materials are employed as matrix for FRPs (Route A in Fig. 3); and (ii) growth or deposition of CNTs on fiber surface [13] (Route B in Fig. 3), the large surface area of nanomaterials makes it possible to improve the interfacial interactions between the fibers and matrix, thus enhance the overall performance of FRPs.

2.3. Mechanical reinforcement

The exceptional mechanical properties along with low density and high aspect ratio of CNTs make them an ideal candidate for reinforcement in composite materials. Following the first paper published in this field [14], significant progress has been made to develop CNT/polymer nanocomposites with multi-functional properties. The mechnical properties of CNT/polymer nanocomposites have been reviewed in several excellent papers [15–17], and a general conclusion is that CNTs can improve simultaneously

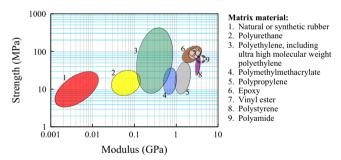


Fig. 4. Strength versus elastic modulus of CNT/polymer nanocomposites.

the modulus, strength and toughness of polymers, which is seldom found in traditional composites reinforced by microscale fillers. For example, CNTs enhanced the elastic modulus, strength and fracture toughness of epoxy by 24%, 20% and 60%, respectively [18]. The reinforcing effects for polymers became more pronounced when CNTs were introduced into some thermal plastics and elastomers [17]. Fig. 4 plots the strength as a function of elastic modulus (both in logarithmic scale) for some typical CNT/polymer nanocomposites. Some requirements, such as proper dispersion, a high aspect ratio and preferential alignment of CNTs, strong interfacial interactions between CNTs and polymer matrix, need to be addressed for effective CNT reinforcement in composites.

In FRPs, the formation and propagation of interlaminar cracks can lead to significant reductions in laminate strength and stiffness. The conditions that favor delamination can range from out-of-plane tensile loads to in-plane compressive loads, poor interficial interaction between the fiber and matrix as well as local transverse low velocity impact. Suppression of delamination is therefore of interest, particularly in primary structures made of FRPs. Table 2 summarizes recent studies reporting improved mechanical properties of FRPs due to the introduction of CNTs [5,19,20]. The results confirmed that the matrix-dominated interlaminar shear strengths (ILSS) of FRPs were improved in the range of 7 to 45% by adding CNTs in various polymers as matrices for FRPs, and the fiber-dominated interfacial shear strengths (IFSS) were also enhanced by more than 30% when CNTs were grown or deposited on fiber surface.

FRP matrix modified by CNTs have been applied to fabricate prototype of wind blade. For example, Applied Nanotech Holdings Inc (ANI) has harnessed its expertise in CNT/polymer enhanced FRPs to develop a strengthened composite that can be used for wind turbine blades and other engineering applications with long life-time requirements [21]. Using a small commercial blade as a template, a team in Case Western Reserve University manufactured CNT-reinforced polyurethane (PU) wind blades [22]. Specifically, CNT reinforced PU blade with length of around 74 cm was fabricated with six glass fiber mats using the vacuum-assisted technique. The blade was substantially lighter, more rigid and tougher than conventional blades. Comparing other reinforcing materials, the researchers found that the CNTs are lighter per unit of volume than conventional fibers and have five times the tensile strength of carbon fiber and more than 60 times that of aluminum.

Besides the primary requirements of stiffness and strength, materials for wind blades must withstand severe fatigue loading under different environments because FRP structures are vulnerable to cumulative damages owing to the cyclic loading in service

| Table 2 | | | | | | |
|----------------|------------|------------|---------|--------|------|------------|
| Improvement in | mechanical | properties | of FRPs | due to | CNTs | [5,19,20]. |

| Strategy | Fiber | Polymer matrix | CNT content (wt%) | Improvement on mechanical properties (%) |
|--|-----------------------------------|-------------------------|-------------------|--|
| Introduction of CNTs in polymer resins | Glass fiber | Ероху | 0.3% | 16 ^a |
| | Glass fiber | Epoxy | 0.015% | 45 ^a |
| | Glass fiber | Epoxy | 0.3% | 20 ^a |
| | Glass fiber | Epoxy | 1.0% | $\sim 7^a$ |
| | Glass fiber | Vinyl ester-epoxy resin | 0.1% | 11 ^a |
| | Glass fiber fabrics | Epoxy | 0.3% | \sim 5^a |
| | Woven glass fiber | Epoxy | 2.0% | 33 ^a |
| | Woven glass fiber | Vinyl ester | 0.1% | 20-45 ^a |
| | Carbon fiber | Epoxy | 0.25% | 27 ^a |
| Growth/deposition of CNTs on fiber surface | Woven carbon fiber | Ероху | N/A | 30 ^b |
| . • | Carbon fiber | Ероху | N/A | up to 475 ^b |
| | Alumni fiber | Ероху | N/A | 69 ^b |
| | Carbon fiber with CNT bucky paper | Ероху | N/A | 31 ^b |
| | Silica fiber | Polymethylmethacrylate | N/A | 80-150 ^b |

^a Interlaminar shear strength measured by the short beam shear test.

^b Interfacial shear strength measured by the single fiber fragmentation test.

life [23]. The fatigue property of material is generally characterized by a cyclic stress (S) against the cycles to failure (N), i.e, S-N curve. The test is mainly used to identify inherently structural defects in composites resulted from either the design or manufacturing process [24]. Fig. 5 shows the effect of CNTs on the fatigue behavior of polymer-based nanocomposites and FRP structures. The incorporation of a small amount of CNTs (\sim 0.2 wt%) increased the fatigue life of epoxy in the high-cycle, low-stress amplitude regime by 1550% (Fig. 5A) [25]. This enhancement was caused by pull-out of CNTs and crack-bridging at the crack interface. In other words. CNTs were effective to suppress the fatigue crack growth in polymer matrix. Using a compliance method. Zhang et al. [26] studied the crack propagation rate as a function of the applied stress intensity factor for the CNT/epoxy nanocomposites, and demonstrated up to an order of magnitude reduction in the crack propagation rate for the nanocomposites with 0.5 wt% CNTs. This reduction exhibited a strong dependence on the weight fraction of nanotubes as well as the applied stress intensity factor, as shown in Fig. 5B. In another work by the same group, the authors studied the effect of CNT dimension and dispersion on fatigue crack growth suppression in the same matrix [27]. They observed that fatigue crack growth rates were significantly reduced by (i) using CNTs with smaller diameter, (ii) increasing the CNT length; and (iii) improving the dispersion of nanotubes. By optimizing the parameters like tube length, diameter and dispersion states, the authors showed an over 20-fold reduction in the fatigue crack propagation rate of the nanocomposites in contrast to the neat epoxy.

Damage mechanisms in conventional FRP structures consist of the formation of cracks in the matrix that initiate and propagate under cyclic loading, eventually causing fiber failure and fracture of the composites. The addition of CNTs has been proven to suppress the initiation and propogation of cracks in polymer resins. Following this concept, a few studies have been devoted to investigate the effect of CNTs on the fatigue life of FRP structures [28-30]. The results from Grimmer et al. [28] showed that the addition of 1 wt% CNTs to the polymer matrix of glass fiber-epoxy composite laminates improved their high-cycle fatigue strength by 60-250% (Fig. 5C), depending on the loading conditions. In addition, real-time monitoring of the hysteresis per cycle during loading confirmed that the overall hysteresis level was lower than unmodified glass fiber composites (Fig. 5D). This observation originated from the facts that (i) incorporation of CNTs into the matrix inhibited the formation of large cracks since a large density of nucleation sites were provided by nanotubes due to their low density and size effect; and (ii) the increase in energy absorption from the fracture of nanotubes bridging across nanoscale cracks and nanotube pull-out from the matrix contributed to the overall fatigue strength and durability of FRPs.

2.4. Environmental issues

It is known that materials for wind blades are vulnerable to some environmental issues, such as lighting, heat, humidity (will be discussed in the following section). Among them, lighting

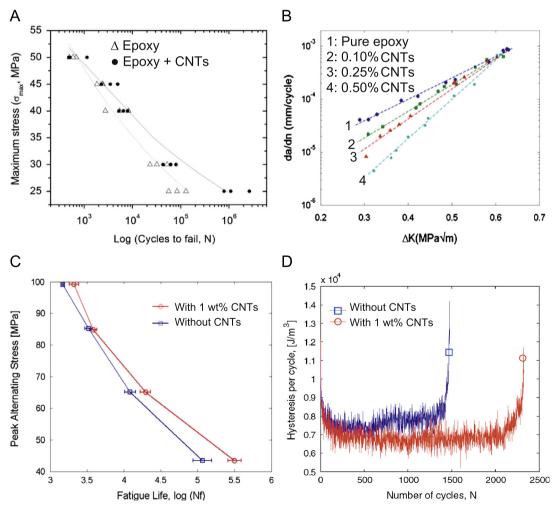


Fig. 5. Fatigue behavior of composites with CNTs. (A: S-N curves of CNT/epoxy nanocomposites; B: Fatigue crack growth rate of CNT/epoxy nanocomposites as a function of applied stress intensity factor; C: S-N curves of FRPs with CNTs; D: Hysteresis observed in FRPs containing CNTs) [25, 27, 28].

strikes have been regarded as one of the worst enemies for wind blades over years [31]. Available status reveals that for the wind turbine installed in Europe, the average number of faults per 100 turbine years is equal to 6, whereas this value can reach as high as 36 in Japan due to the severe winter lighting parameters [32]. The increasing number and height of installed turbines have resulted in an incidence of lightning damage greater than anticipated with repair costs beyond acceptable levels. Therefore, the lighting protection is quite crucial and the best available protection methods need to be considered for wind blades.

Currently available lightning protection system consists of lightning receptors at the tip or surface of the blade, as schematically shown in Fig. 6A [31]. Inside the blade there are conductors (metallic meshes or wires) connected to the receptors. Via the conductors, lightning current and thermal energy caused by lightning strikes can be dissipated. A limited area of the receptors leads to a relatively small safe contact surface for the lightning stroke (few square centimeters) compared to the whole blade surface (e.g., $100 \, \mathrm{m}^2$). In addition, the current involved in a typical strike is so high ($> 30 \, \mathrm{kA}$) that the resulting heat may cause the material of the lightning receptors to vaporize and be removed from the blade. The employment of metallic materials brings additional problems like the poor compatibility between metal and polymer resin, the increase in weight and cost of blades.

Novel concept focusing on improving lightning protection for wind blades is to use materials with multi-functional properties. CNTs have great potential to achieve this goal, specifically due to the following advantages: (i) CNTs exhibit a high electrical conductivity to efficiently divert the lighting currents; (ii) CNTs provide excellent chemical and thermal stability to sustain the heat arising from the lightning discharge; (iii) The high thermal conductivity of CNTs make it possible to dissipate the heat generated from the lighting strikes. By depositing a very thin layer of CNTs on glass fibers, Gao et al. [33] prepared functional fibers with the highest electrical conductivity of 10⁶ S/cm, which is comparable to that of metals. This result shows the potential of employing CNTs as a conducting coating for wind blades to transport lighting current. Recently, a published patent [34] described the employment of CNTs as lighting receptors for wind blades. The receptors integrated onto the wind blades ensured that blade materials were able to withstand the electrical and thermal shocks arising from lighting strikes.

Carbon fibers have been applied with varying degrees of success for lighting protection for FRPs because of their excellent electrical and reasonable thermal conductivity. However, the

polymer matrix isolates and insulates adjacent bundles of fibers in CFRP structures. The introduction of CNTs into epoxy matrix offers a way to improve the matrix electrical conductivity and possibly to connect the carbon fibers both within and between the plies. Fig. 6B shows the maximum electrical conductivity of CNT/ epoxy nanocomposites [35]. It should be noted that depending on the type and dispersion states of CNTs, the conductivity of nanocomposites varies significantly and can be controlled, suggesting the versatilities of CNT/polymer nanocomposites for wind blade materials, which may satisfy some additional requirements like electromagnetic shielding, conducting adhesives, coatings and films, electrostatic discharge, thermal interface control, and so on.

The guaranteed long lifetime of wind blades requires the constituent materials to exhibit excellent thermal properties to resist the thermal impacts either from the sunlight or from the seasonal variation. The incorporation of CNTs in a polymer can also rectify the thermal stability (including thermal shrinkage, glass transition temperature, melting and thermal decomposition temperatures) as well as flame-retardant properties through their constraint effect on the polymer segments and chains [17]. It was reported [36] that CNTs outperformed nanoclays as effective flame-retardant additives if they formed a jammed network structure in the polymer matrix. Again, these properties are very important when blades are under the lighting strikes, as the lighting may cause a fire to the blades.

2.5. Barrier performance

The barrier performance refers to the property of material when specified permeable object transmits from high density side into low density part. The transmitting process includes adsorption/desorption, dissolution, diffusion, and so forth. In polymer system, the sorption and diffusion of gas and water molecules can plasticize the resin and decrease their mechanical response. Therefore, barrier performance of resin is an important consideration when selecting material for wind blades, especially for these installed in inshore and high humidity areas.

Previous studies indicated that the introduction of nanofillers with large aspect ratios (clay, exfoliated graphite) into polymers can cause the diffusing molecules, such as gas, moisture and chemicals, to travel around the nanoparticles through substantially longer paths, leading to a significant improvement on the barrier resistance of polymers [37–39]. The small size and high aspect ratio of CNTs make these materials possible to rectify the

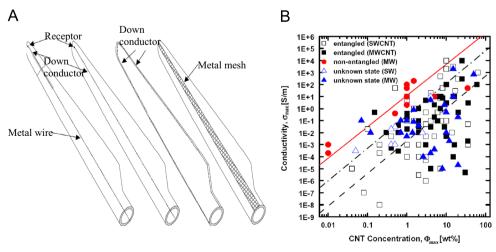


Fig. 6. (A) Lightning protection for large modern wind turbine blades [31]; and (B) maximum electrical conductivities of CNT/epoxy nanocomposites prepared by using single- or multi-walled CNTs (SWCNT/MWCNT) with different dispersion states [35].

barrier properties of polymers as well. Khan et al. [40] prepared CNT reinforced polycaprolactone (PCL) nanocomposites using compression molding method, and found that the water vapor permeability of PCL was decreased from 1.51 to 1.08 g mm/m² · day with 0.2 wt% CNTs. The enhanced barrier properties of polymer nanocomposites are not limited to the thermoplastic matrices. Indeed, the introduction of CNTs in thermosetting resins, like epoxy, a commonly used polymer matrix for wind blades, can inhibit the diffusion and sorption of water vapor in matrix. By measuring the increase of weight with time for samples exposed to the water vapor at a given partial pressure. Guadagno et al. [41] studied the effects of CNTs on the transport properties epoxy. The results showed that the sorption curves of water in epoxy follow the Langmuir sorption behavior, in which the sorption of the vapor molecules occurs on some specific sites. The interaction between CNTs and epoxy matrix can remove the occupancy of these sites by water molecules, decreasing the equilibrium concentration of water in epoxy, thus improve the barrier resistance of nanocomposites to water.

Glass fibers have been widely used as reinforcements in FRP structures for wind blades. It is known that glass fibers are susceptible to moisture and/or alkali conditions because of the hydrolysis of -Si-O-Si- structures. One of the best ways to overcome this problem is to apply a polymer coating that can act as barrier on the glass fibers [39]. Ma et al. [42] studied the barrier properties of glass fibers coated with epoxy-based nanocomposites containing CNTs and graphene. The tensile strengths of glass fibers with different coating measured before and after ageing in alkali solution are compared in Fig. 7A. All glass fibers showed gradual losses in strength with increasing ageing time, indicating fiber degradation due to the attack by moisture and alkali ions. The reductions in strength were in general much more significant in the fibers without nanocomposite coating than those with. For example, the fibers with epoxy coating maintained about 70% of the original strength after 5 days of ageing, which was lower than their counterparts with 77% and 87% retention with CNT/epoxy and graphene/epoxy coating, respectively. Under the longer time of ageing, say 10 days of immersion in alkali solution, the strength of fiber yarns with coating containing graphene outperformed their counterparts with CNT/epoxy and neat epoxy coating, and over 80% of the original strength was maintained in contrast to about 55% of retention found in other fibers. Based on above results, the authors concluded that the dimension of nanoparticles in nanocomposite coatings plays an important role in governing the barrier performance of fibers. The modification of fiber coatings using nanoparticles would delay the penetration of environmental attacks towards the fiber surface, as schematically shown in Fig. 7B: For the neat epoxy coating, the water molecules and alkali ions can easily diffuse and penetrate through the polymer and reach the fiber surface, causing substantial damage to the fibers. This penetration was diminished for the fibers with CNT/epoxy coating, as CNTs can act as a heterogeneous material in polymer matrix, blocking the traveling/diffusion of moisture and chemical in the coating layer. The barrier capability was significantly enhanced for the fibers with graphene/epoxy coating because the plate-like structure of graphene forces the moisture/alkali ions to travel tortuous and longer ways to reach fiber surface, resulting in the protection of fiber surface and consequent improved barrier resistance.

2.6. Defect monitoring in FRP structures

The specific discrete build-up of FRPs (laminate or sandwich) makes maintenance and damage analysis of these materials a challenging task. As these composites are sensitive to the damages arising from delamination and matrix cracking, a reliable method for the detection and assessment of defects in FRPs is critical to optimizing their maintenance, reducing downtime and mitigating the risk of implementation. Furthermore, an in-situ monitoring of curing and damage development in composites could be a useful tool to evaluate their reliability and lifetime [43].

Scanning acoustic microscopy (SAM) is a highly developed method to investigate the defects in FRPs. The velocity and attenuation of an ultrasonic pulse passing through composites provide information about structural defects [44]. This technique suffers from the illustration of crack initiation and propagation in composites under mechanical loads. By embedding conventional health monitoring sensors, such as optical fibers [45] and shape memory alloys [46], it is possible to monitor the structural defects in composites. However, there are large stress perturbations caused by weak interfacial adhesion with polymer matrix and large diameters of fibers.

The use of CNTs as a sensory material has emerged as one of the most promising fields for practical applications. Among various sensory applications, the employment of CNTs for health monitoring of FRP structure is a very new research area. Ongoing studies are mainly concentrated on the measurement of structural deformation of FRP matrix consisting of CNTs and polymers. Fiedler et al. [47] first proposed this concept by studying the electrical response of CNT/epoxy nanocomposites under

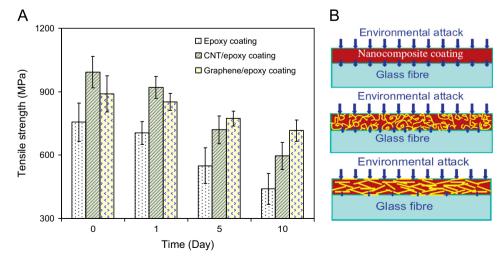


Fig. 7. Barrier properties of glass fibers with CNT/epoxy nanocomposite coating. (A: Tensile strength of glass fibre yarns measured after ageing in alkaline solution; B: Schematic of alkali ions and moisture diffusion through different coatings: Top-neat epoxy coating; Middle-CNT/epoxy coating; Bottom-graphene/epoxy coating) [42].

mechanical load, and illustrated that the conductive modification of nanocomposites can be applied for both strain and damage sensing of materials. Thostenson and Chou further developed this technique and fabricated the composites reinforced with conventional glass fibers and CNTs [48]. The results showed that CNTs can penetrate the matrix-rich areas between fibers in individual bundles as well as between adjacent fiber plies (Fig. 8A) and can

achieve a nerve-like network throughout the arrays of fibers in a composite. The authors also demonstrated that the CNT networks formed in epoxy were remarkably sensitive to the initial stages of matrix-dominated failure and can detect damage in-situ. Through experiments design and optimization, it is feasible to identify the onset, nature, and evolution of damage in FRP structure by using direct-current measurements (Fig. 8B).

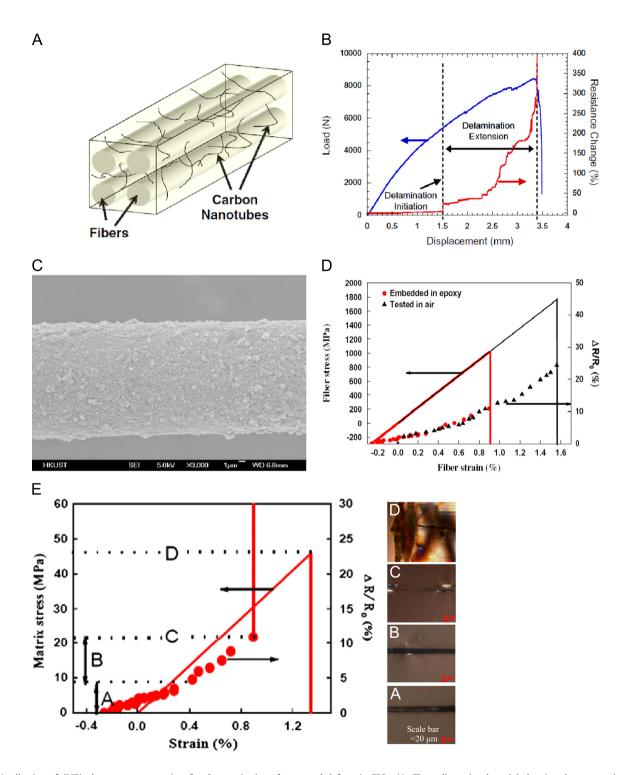


Fig. 8. Application of CNT/polymer nanocomposites for the monitoring of structural defects in FRPs. (A: Three-dimensional model showing the penetration of CNTs throughout a fiber array; B: Load/displacement and resistance responses of a composite; C: Single glass fibres coated with CNT/epoxy nanocomposites; D: Changes in fibre stress and electrical resistance as a function of fibre tensile strain for fibres with CNT/epoxy coating; E: Birefringence patterns of single glass fibre coated with CNT/epoxy in FRP under different loading conditions and corresponding electrical resistance change) [48, 54].

One of the common features among the sensory applications of CNT/polymer nanocomposites is that the mechanical loads applied on the materials will result in the changes on the electrical resistance of nanocomposites. In fact, this idea is a continuation of employing electrical techniques as a non-destructive way to monitor the damages in CFRP under static and dynamic loading conditions. The principle of this technique lies in that carbon fibers are conductive and Raman-sensitive, the fracture of fibers results in the change in electrical/Raman response of composites [49,50]. However, this approach does not applicable to the composites with non-conducting fibers (e.g., glass or aramid fibers). Different techniques have been proposed to overcome this problem. One method is to employ Raman-sensitive fibers as a health monitoring sensor among the neighboring Raman-insensitive reinforcing fibers [51]. Glass fibers coated with Raman-active materials, such as polydiacetylene [52] and CNTs [53], were also employed to map the strain distribution on the fiber surface in FRP structures.

More recently, Liu and Ma [54] presented the development of glass fibers coated with nanocomposites consisting of CNTs and epoxy (Fig. 8C). Single glass fibers with nanocomposite coating were embedded in a polymer matrix as a strain sensor for FRPs. Raman spectroscopy and electrical response of glass fibers under mechanical load were coupled for in-situ sensing of deformation in composites. The introduction of CNTs offered a possibility to make the Raman and electrical responses of the coated glass fibers sensitive to mechanical loading, whereas the epoxy functioned as an interface to transfer the load from the polymer matrix to fibers. The results showed that the fibers with nanocomposite coating exhibited efficient stress transfer across the fiber-matrix interface. A relationship between the fiber stress and the change in electrical resistance against the fiber strain either in air or embedded in composites was established (Fig. 8D). In addition, the authors studied the birefringence patterns of FRP containing single fiber with CNT coating under the tension state. Four different stages are identified, as shown in Fig. 8E: Stage A represented the linear relationship between the change in resistance and fiber strain. Stage B corresponded to the period when the resistance changed abruptly due to the disruption in the CNT networks on the fiber surface. This observation was accompanied by a weak birefringence pattern around the stretched coating layer arising from the partially unstable CNT networks. Clear birefringence patterns were observed in Stage C, where the fiber was fractured, resulting in a surge in electrical resistance to infinity at a net fiber strain of about 0.9%. The image at Stage D was obtained after matrix fracture. It is worth noting that the fiber was broken before matrix fracture, suggesting that the fiber with a nanocomposite coating can be employed as a sensor to offer an early warning of fracture in a FRP structures.

3. Conclusions and perspectives

Significant progress has been made to develop CNT/polymer nanocomposites, however, their applications in wind energy are in the infant stage of realization. In this paper, a systematic overview on the perspectives of CNT/polymer nanocomposites for wind blades is provided. The suitabilities of these nanocomposites are analyzed with considerations on the structural and functional requirements for blade materials. It is demonstrated that CNT/polymer nanocomposites, which can be applied either as a matrix for FRP structures or as a coating/sizing for fiber, have great potential to optimize blade materials to be much stiffer, stronger, and have better fatigue resistance. The multi-functional properties of CNT/polymer nanocomposites offer a new concept to address the problems associated with lighting strikes, thermal shocks and humidity for blade materials in service life. The employment of CNT/polymer nanocomposites for

monitoring the damage development in FRP structures is a promising way to evaluate the reliability and lifetime of blades.

Even with the well established understanding on the preparation and property of CNT/polymer nanocomposites, there are many fundamental issues and challenges need to be addressed for their applications in wind blade materials. They include, but are not limited to, the following aspects:

- (i) Poor CNT dispersion and interfacial interactions with polymer resins have been identified as two major obstacles in developing high-performance materials. Efforts aiming at enhancing the solubility and dispersion of CNTs in polymers and improving the interfacial adhesion between CNTs and various polymers must be addressed before CNT/polymer nanocomposites can be applied in real blade products. In addition, there is a concern that dispersed CNTs exhibit a tendency to re-agglomerate, therefore, the stabilization of dispersed CNTs in polymers becomes crucial as resin systems for blades must satisfy the requirements on the viscosity and long pot-life for processing.
- (ii) The relatively high cost of CNTs limits their applications in FRP structures for wind blades. Hybridization of CNTs with other lower cost fillers, such as carbon black, clay, offers an alternative to lower the cost of CNT/polymer nanocomposites. However, proper dispersion of these hybrid fillers into a polymer matrix is a challenging task because these hybrid fillers have their specific dimensions and different dispersion characteristics.
- (iii) Very low concentration of CNTs in polymers can drastically change the properties of CNT/polymer nanocomposites. Progress has been made to simulate these nanoscale effects using micromechanics and atomic/molecular dynamics methods. These methods may not applicable for FRP structures containing CNTs because the reinforcements in the system consist of microscale fibers and nanoscale CNTs. Fundamental studies in this field, such as modeling and prediction taking into account of the filler-filler and filler-matrix interactions, filler alignment and dispersion, will provide practical guidelines for the optimization of material properties for wind blades.
- (iv) Fabrication of FRP structures by impregnating conventional fibers with CNT/polymer nanocomposite matrix is relatively simple and can be readily applied in current setups for blade manufacturing, however, this route is limited to a low content of CNTs in polymers. New approaches/modifications are needed to avoid the problems associated with the increasing rheology/viscosity of resins with higher CNT content.
- (v) The polymer matrix used in wind blades are generally thermosetting resins, and these materials have always presented a problem to recycling. This limitation requires various techniques to repair damaged parts in FRP structures for seeking longer service life. CNT-based nanocomposites offers a way to achieve this goal due to their multi-functioalities and compatibility with resin. Design and optimization of technique for repairing the damaged parts in blades using CNT/polymer nanocomposites will be an applicable practice to extent their lifetime. In addition, replacement of thermosetting resins using CNT/thermoplastic nanocomposites with comparable properties offers a possible way to develop green wind blades sustainable to the environment.

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